PR-34. TRANSITION METAL-FREE REGIOSELECTIVE CROSS-COUPLING OF AZINE N-OXIDES WITH CYMANTRENYL LITHIUM

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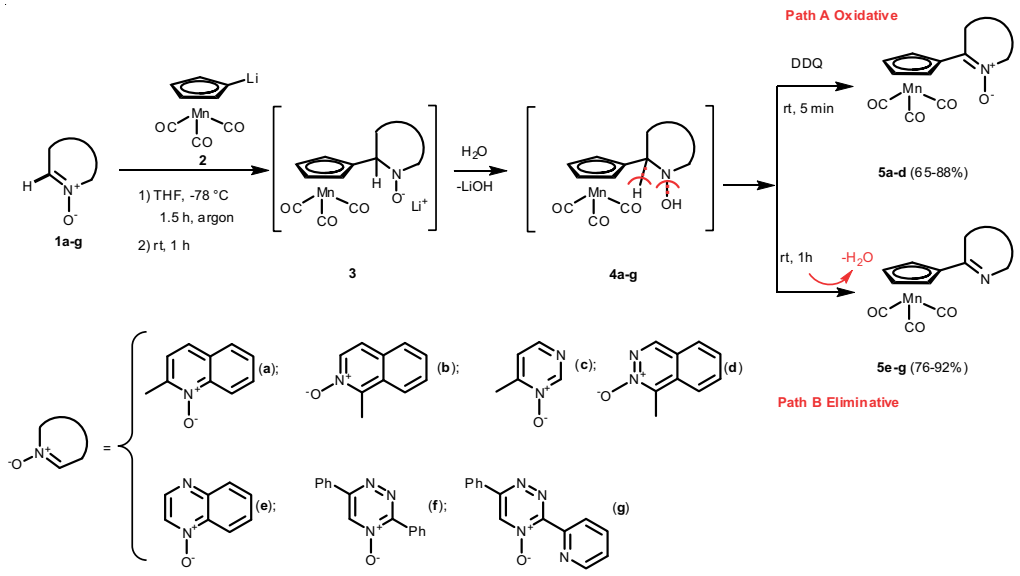
It is known, that cyclopentadienyl manganese (I) tricarbonyl (cymantrene) takes the next place after ferrocene and ruthenocene in the list, counting number of experimental works in bioorganometallic chemistry. Unique electronic properties and a high IR activity of CO-groups allow one to use cymantrenes as analytical labels for immunoassays, electro- and photochemical processes, as components of initiating mixtures for polymerization vinyl monomers, as well as in bioorganic chemistry and drug design. At the same time, there are a limited number of methods to prepare azinyl cymantrenes. They include such principal approaches, as transition metal-catalyzed cross-coupling reactions of organoelement compounds with heterocyclic halides (or pseudo halides), construction of a heteroarene ring on cymantrene scaffolds, and the direct metal-free (non-catalyzed by transition metals) cross-dehydrogenative coupling (CDC) reaction of azines with the cymantrenyl lithium.

For the first time we wish to describe use of the transition metal-free cross-coupling reaction for modification of the structure of azine N-oxides (an activated form of azaaromatics) through their reactions with cymantrenyl lithium.



The azinyl cymantrenes can be obtained in good yields under mild reaction conditions. It has been found that aromatization of intermediate σ^H-adducts depends on the structure of the starting azine N-oxides, and can be realized in both oxidative and eliminative modes.

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